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The objective of this program was the development of novel OMCVD/LCVD processes for preparation of wide band-gap III/V semiconductors and the elucidation of the basic reaction mechanisms in these processes, so as to control the deposition rates and to improve the opto-electronic properties of the materials.

The synthesis and the mechanistic elucidation of wide band-gap III/V metal nitrides by OMCVD and LCVD, the dry-passivation of GaAs and the deposition of carbon nitride films, have been carried out with a unique UHV surface reaction system equipped with multiple gas-phase and surface species analyses. The system was constructed with joint support from the ONR and Emory University.

Gas-phase species were detected by EI- and REMPI-MS, whereas surface species and structures were characterized by multiple surface diagnostic tools: AES, UPS, XPS, LEED, SEM and HREELS. The systematic elucidation of the spectroscopy and the mechanisms for the thermal and photochemical decomposition reactions of individual source molecules involved in the OMCVD/LCVD processes were first carried out before the actual deposition processes were conducted.

We used a new nitrogen source, hydrazoic acid (HN₃), for the preparation of InN films with 1:1 elemental ratio by low-pressure CVD. The prepared films were characterized by AES, UPS, XPS, SEM, LEED and HREELS, and optical techniques such as UV/visible adsorption and photo-luminescence. InN films with very high quality SEM and UPS characteristics have been deposited on GaAs substrates without a buffer layer. Over 20 technical papers (with 23 presentations) were completed from these studies.

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and Surface Diagnostics"**

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by

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SUMMARY

Future information processing lies in the direct, fast coupling of photons and electrons using wide band-gap semiconductors. This is one of the most important aspects of current microelectronic R&D efforts. The objective of this program focused on the development of novel OMCVD/LCVD processes for preparation of wide band-gap III/V semiconductors as well as the elucidation of the basic reaction mechanisms involved in these new processes, so as to control the deposition rates and to improve the opto-electronic properties of the prepared materials.

The synthesis and the mechanistic elucidation of wide band-gap III/V metal nitrides by OMCVD and LCVD, as well as the dry-passivation of GaAs and the deposition of carbon nitride films, have been carried out with a unique UHV surface reaction system equipped with multiple gas-phase and surface species analyses. The system was constructed with joint support from the ONR and Emory University.

Gas-phase species were detected by EI- and REMPI-MS, whereas surface species and structures were characterized by the combination of multiple surface diagnostic tools: AES, UPS, XPS, LEED, SEM and HREELS. The systematic elucidation of the spectroscopy and the mechanisms for the thermal and photochemical decomposition reactions of individual source molecules involved in the OMCVD/LCVD processes were first carried out before the actual deposition processes have been conducted. In this manner, basic data were available for the improvement of the deposition processes and the performance of the new materials.

We have succeeded in using a new nitrogen source, hydrazoic acid (HN_3), for the preparation of InN films with 1:1 elemental ratio by low-pressure CVD. HN_3 can be prepared in large quantities with high purity. The prepared films were characterized by AES, UPS, XPS, SEM, LEED and HREELS, as well as the optical techniques such as UV/visible adsorption and photo-luminescence. It is useful to note that InN films with very high quality SEM and UPS characteristics have been deposited on GaAs substrates without a buffer layer. The technique will be employed for wider bandgap GaN and AlN deposition.

Over twenty technical papers (with twenty-three presentations) have been completed from this series of studies.

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I. INTRODUCTION

In recent years, the synthesis of high quality compound semiconductors by organometallic chemical vapor deposition (OMCVD) and laser chemical vapor deposition (LCVD) has made substantial strides through the use of better organometallic source molecules and the improved surface/interface diagnostics to monitor the kinetics of film growth and the elimination of impurity incorporation during the growth process.

Preparation of semiconductive films, as in the synthesis of complex organic or inorganic compounds, requires a clear understanding of the mechanism involved in the deposition process and, particularly, the key reaction steps which control the rate of film growth. In order to achieve this goal, we have in the past two years extensively utilized a UHV surface reaction system, which is equipped with multiple laser and surface diagnostics (XPS, UPS, AES, LEED and HREELS) for the systematic studies of the surface chemistry of individual source molecules on a growing substrate surface to gain better understanding of the thermochemical and photochemical mechanisms involved in the decomposition of these molecules on the surface. Mechanistically, these reactions differ greatly from those occurring in the gas phase; a thorough study of their reaction mechanisms is naturally called for, prior to practical deposition of a desired film.

In this ONR-funded project, our main focus has been placed on the search for a more facile and clean source of nitrogen for the deposition of group III nitrides which, because of their large band gaps (2-6 eV) and the possibility of varying the gap size by means of mixing the group III metals, have a great potential for visible and ultraviolet opto-electronic devices. We have found by a series of studies on the decomposition of N_2H_4 , $\text{CH}_3\text{N}_2\text{H}_3$, NH_2CHO , and HN_3 on Si single crystal surfaces using different surface diagnostic tools that HN_3 is by far the cleanest and most labile N-source. We have demonstrated through the preparation of InN films, which are known to be more difficult to grow than other nitride films, such as GaN, due to the high vapor pressure of InN which precludes high-temperature deposition with ammonia. The combined use of HN_3 and laser excitation of the depositing surface, however, allows us to prepare high-quality InN films on Si with 1:1 elemental ratio at temperatures as low as 300 K! In addition, patterning, i.e., selective growing of InN on the substrates becomes feasible by exciting with the laser beam. The effect of laser excitation, as illustrated by the result of a separate experiment on the photodissociation of HN_3 adsorbed on both Si(100)

and Si(111) surfaces, results from the efficient removal of H atoms from reactive N-sites:



these active sites interact strongly with In atoms or In-containing radicals to form InN.

We believe that the approach should be equally efficient for the deposition of higher band-gap nitride films. We plan to extend the method, using HN_3 as the N-source with UV photon beams of differing wavelengths to enhance growth rates, for the deposition of AlN, GaN and other nitrides which are known to be excellent insulating materials, e.g., BN, TiN and Si_3N_4 .

II. ACCOMPLISHMENTS

In this project (Dec. 1, 1988-Sep. 30, 1993) a significant amount of data have been acquired in both fundamental surface chemistry and practical film deposition studies. The results of these systematic studies, aiming toward the practical aspect of semiconductor film preparation for opto-electronic applications, are briefly summarized as follows:

A. Surface Chemistry of TMIIn on Si

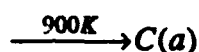
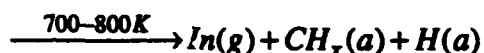
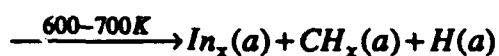
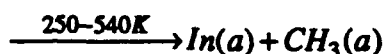
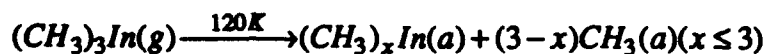
Trimethyl indium (TMIIn) is a common organometallic source in the CVD processes of InP, InN and $\text{In}_x\text{Ga}_{1-x}\text{N}$ etc. In-containing semiconductive materials, surprisingly little is known concerning the behavior of TMIIn on heated substrates. We have recently investigated the adsorption and thermal decomposition of TMIIn on Si single crystal surfaces.

TMIIn/Si(111)^{5}*

When a 2-L TMIIn was dosed on a Si(111)-7x7 sample, peaks at 63, 88, 154, 181 and 368 meV, due to In-C stretching, CH_3 rocking, CH_3 symmetric deformation, CH_3 asymmetric deformation and C-H stretching vibrations, respectively, were detected. The relatively weak 63 meV peak and strong 86 and 181 meV peaks suggest a partial dissociation of the In-C bonds. When the sample was annealed at 250 K, the further dissociation of In-C bonds was indicated by the attenuation of the 63 meV peak in HREELS and the 3.7 eV peak in UPS. Both peaks disappeared at 540 K and a peak at 105 meV due to CH_3 attached to the surface appeared in HREELS, because In-C bond breaking was complete at this temperature. The shifts of the In_{3d} and In_{4d} peaks in

*The superscript refers to the publication number given in section (III).

XPS and UPS, respectively, are likely due to the In islands formation on the surface at ~600K. Meanwhile, the appearance of the Si-H stretching mode at 257 meV in HREELS obviously indicates a breaking of the C-H bond. Above 690 K, In desorbs from the surface, while the breaking of the C-H bond and the desorption of the H species are completed at $T_s \geq 900$ K. The thermal decomposition process of TMIn on Si(111) can be summarized as:



TMIn/Si(100)¹⁰

Similar studies were carried out for TMIn on Si(100)-2x1. The HREELS of 1 L TMIn on Si(100)-2x1 at 110 K taken in (a) the specular and (b) 12° off-specular modes indicated that the relatively strong 62 meV peak due to the In-C stretching vibration suggests the In-C bond breaking occurred to a lesser extent upon the adsorption of TMIn on Si(100) than on Si(111) and Si(110). On the other hand, the near absence of this mode in the off-specular spectrum indicates that the 62 meV mode is mainly due to dipole-scattering, which in turn suggests either a dissociatively or a non-planar adsorption of TMIn on the surface. This could be caused by the interaction between the empty 5p_z orbital in In and the dangling bond of the surface atom by sharing the electrons from the latter. The involvement of the surface states upon the adsorption of TMIn was clearly revealed in the He(I) UP spectra. In the case of TMIn on Si(111)-7x7, the 0.2 eV peak due to S₁ surface states (originated from the adatoms) attenuated first and then the 0.8 eV peak due to S₂ surface states (originated from the rest atoms) started to decrease at $D \geq 0.3$ L.

TMIn/Si(110)⁸

Si(110) surface is often used as the substrate for film deposition, because it has a relatively open surface structure so that foreign particles can penetrate into the subsurface. Furthermore, the large number of unsaturated dangling bonds and atomic defects existed on Si(110) makes it chemically more reactive towards some molecules than Si(111) and Si(100) do. To study the substrate effect on the thermal decomposition process of TMIn, we have investigated the interaction between TMIn and Si(110). The HREELS of TMIn on all three surfaces taken under the essentially same experimental conditions revealed the weaker In-C stretching mode for TMIn on Si(110), indicating that the breaking of the In-C bond to a larger extent for TMIn on Si(110) than on the other two surfaces. Such a difference was further established by the annealing effect. At 250 K, the 61 meV peak virtually disappeared for TMIn on Si(110), but only attenuated to some extent in the cases of Si(100) and Si(111).

Another interesting observation is that more In species survived on Si(110) than on Si(100) or Si(111) at ~800 K. This is revealed on XPS which clearly showed the presence of the $\text{In}_{3d\ 5/2}$ peak. While in the corresponding XPS measurements for TMIn on Si(100) or Si(111), the In XPS signals were much weaker at $T_s \geq 800$ K. These observations suggest that In atoms bond more strongly to the Si(110) surface, presumably to the surface defect sites, or penetrate into the subsurface on Si(110).

B. Surface Chemistry of $\text{N}_2\text{H}_4/\text{CH}_3\text{N}_2\text{H}_3$ on Si

N_2H_4 has been demonstrated to be very a effective molecular nitriding agent for CVD of Si_3N_4 and III-V nitrides because of its high chemical reactivity. However, little is known about the reaction mechanism of N_2H_4 on Si substrates. We have studied the surface chemistry of N_2H_4 on Si substrates.

N_2H_4 /Si(100)-2x1¹⁵

The thermal effects on N_{1s} XPS has been studied. At lower N_2H_4 dosages (<0.4 L), a partial dissociation of NH bonds was indicated by the 399.0 eV peak, which became a lower energy tail as the dosage was increased. This NH bond breaking upon the adsorption of N_2H_4 on Si (100) at 100 K was confirmed by the appearance of the Si-H stretching mode at 255 meV in HREELS. Other peaks in HREELS are attributable to the N_2H_4 molecular vibrations. The NH bond breaking continued as the sample was annealed at 220 and 450 K. At 600 K, the breaking of NN bond occurred and the dissociation products NH_x ($x = 0, 1, 2$) were identified on the surface. The NN stretching mode at 138 meV virtually disappeared and the NH_2 deformation and the

NH stretching modes shifted from 200 and 413 to 192 and 420 meV, respectively. The same conclusion can also be established from the corresponding XPS and UPS results. Above 800 K, only N remained on the surface to form Si nitride after the complete dissociation of the NH bond and the desorption of the H species.

N₂H₄ and CH₃N₂H₃ /Si(111)-7x7

The adsorption and thermal decomposition of N₂H₄ and CH₃N₂H₃ on Si(111)-7x7 were investigated using XPS, UPS and HREELS in the 120-1350 K surface temperature range. Both molecules were partially dissociated into N₂H_x or CH₃N₂H_x (x=2,3) species with the N-N bond parallel or nearly parallel to the surface plane as they adsorbed on the surface at 120 K, especially at lower dosages (e.g., <0.2 L) and more so for N₂H₄ than CH₃N₂H₃. The partial dissociation of NH bonds was indicated by the appearance of the Si-H stretching mode at 255 meV in HREELS and by the relatively larger FWHMs of the N_{1s} XPS (~2.3 and 1.9 eV for N₂H₄ and CH₃N₂H₃, respectively) and the n⁺, n⁻ molecular UPS peaks. When a ~0.4 L N₂H₄ or CH₃N₂H₃ dosed sample was annealed to ~500 K, a significant desorption of the adsorbates occurred as well as the further dissociation of the N-H bonds. At 650 K, the N-N bond started to break for both molecules. The 134 meV peak for N-N stretching vibration in N₂H₄ vanished in HREELS, the N_{1s} XPS peak shifted to 398.7 eV due to the NH_x species and the UPS spectra were dominated by peaks at 4, 7 and 10 eV below E_F. These three peaks are due to NH_x adspecies in consistence with those reported previously in the studies of NH₃ on Si substrates. At ~730 K, the C-N bond dissociated to form CH_x on the surface in the case of CH₃N₂H₃. Further annealing of the sample caused complete breaking of the N-H and CH bonds, the desorption of the H-species and the formation of Si₃N₄ or a mixture of Si-nitride and Si-carbide for N₂H₄ or CH₃N₂H₃, respectively.

C. Surface Chemistry of HCN/DCN on Si

HCN/DCN Si(100)-2x1

We have investigated the spectroscopy and reaction of HCN(DCN) adsorbed on Si(100)-2x1 at T_s ≥ 100 K. HCN(DCN) formed dimers and/or polymers on the surface at 100 K and higher dosages (D > 4L) as clearly indicated in HREELS by the 28 meV peak due to the intermolecular torsional vibration. The HREELS spectrum obtained after warming a 4.5 L HCN dosed surface to 220 K resembles that obtained with a lower HCN dosage (D < 0.6 L) at 100 K. Two major species, HCNH and CN, could be

identified from this spectrum. The former species showed peaks at 160, 368 and ~400 meV for CH=NH, CH and NH stretching vibrations, respectively, while the latter showed a peak at 263 meV due to the C≡N stretching mode. According to a quantum chemical calculation by Melius, the NCNH radical has frequencies at 190, 364 and 407 meV for the aforementioned three stretching vibrations. In the corresponding DCN experiment, the DC=ND stretching mode was observed at 124 meV. Annealing the sample at 560 K appeared to cause the reorientation of the CN radical from an end-on to a side-on adsorption geometry as evidenced in HREELS, UPS and XPS analyses. The C≡N stretching mode at 263 meV in HREELS attenuated, while the intensity of the 6 eV peak due to the CN radical in UPS increased and no intensity decrease was observed for the C_{1s} XPS peak. At 600-800 K, the breaking of NH and CN bonds occurred on the surface. Above 1000 K, a mixture of Si carbide and Si nitride was formed after the complete dissociation of CH, NH and CN bonds and the desorption of H species.

HCN(DCN)/Si(111)-7x7¹³

The interaction of HCN(DCN) with Si(111) was studied with HREELS, UPS and XPS. HCN(DCN) formed dimers and/or polymers on the surface at 100 K with higher dosages ($D > 4$ L). Above 200 K, CN radicals in an end-on adsorption geometry were indicated by the strong 265 meV peak for both HCN and DCN HREELS. Since there is no strong Si--D peak (~200 meV) at this temperature, the other product is presumably HCNH (DCND) species. Such a species was clearly identified on the Si(100) surface. However, the HCNH characteristic features were weak in the HREELS of HCN on Si(111). In the corresponding He(II) UPS measurements, the peak at ~13 eV due to N-H and C-H species nearly disappeared above 220 K. These observations indicate a partial desorption of the HCNH species from Si(111). The different behaviors of HCN on Si(100) and Si(111) can be ascribed to the different topologies of the two surfaces.

D. Surface Chemistry of HN₃ on Si

Hydrazoic acid (HN₃) has been used successfully for the first time as a nitrogen source for CVD of Si nitride and III-V nitrides. It has been demonstrated that the temperature required for Si nitride thin film growing can be lowered by using HN₃ instead of NH₃. We have investigated the adsorption and thermal dissociation of HN₃(DN₃) on Si(100), (110) and (111) as well as the photodissociation of HN₃ on Si(111) and Si(100).

HN₃(DN₃) Si(110)³

When 1.2 L DN₃ was dosed on the surface, peaks at ~70 (shoulder), 128, 158, 270 and 307 meV were observed. These peaks could be attributed to the DN₃ deformation, DN bending, N-N₂, NN≡N and ND stretching vibrations, respectively. When the sample was annealed to higher temperatures, the desorption as well as the partial dissociation of the adsorbates occurred. At 580 K, the DN₃ molecular characteristic features vanished, instead DN_x (x=0,1) species became the dominant adspecies as indicated by the Si-ND_x and DN stretching modes at ~100 and 320 meV, respectively.

The weaker peaks at ~270 and 425 meV are due to the Si-H and NH stretching vibrations indicating that the H-D exchange occurred in the system. Further annealing the surface caused the breaking of ND(NH) bond and the desorption of D(H) species, while N remained on the surface forming Si nitride.

HN₃(DN₃) on Si(111)⁹

The thermal stability and spectroscopy of HN₃(DN₃) on Si(111)-7x7 were studied using HREELS, XPS, AES, UPS and LEED. The results are similar to those observed on Si(110). HN₃ molecularly adsorbed on Si(111) at 120 K and formed dimers at higher dosages (> 2 L). At 270 K, HN₃ started to dissociate into N₂ and NH species, which further dissociated into N and H on the surface between 270 and 800 K. At T_s > 800 K, Si₃N₄ was formed as confirmed by all spectroscopic results, including LEED which showed an 8x8 pattern.

A series of XP spectra have been taken from a 12 L HN₃ on Si(111) sample dosed at 120 K and annealed at the indicated temperatures. At 120 K, two major peaks at 404.1 and 400.3 eV were observed and the latter peak can be deconvoluted into two peaks at 400.8 and 399.8 eV with equal intensities and the same FWHM. These three peaks originated from N^{II}, N^{III} and N^I atoms in HN^IN^{II}N^{III}. Furthermore, a weak peak at ~397.5 eV could be attributed to a small amount dissociated product NH_x (x=0,1). This peak grew a little when the sample was warmed to 270 K. Meanwhile, the total N_{1s} peak intensity decreased by about three times due to a partial desorption of the adsorbates. Above 640 K, the N_{1s} XP spectrum was dominated by a single peak at 397.5 eV, which obviously indicates the dissociation of the HN₃ molecules.

The corresponding He(II) UPS results indicated that both S₁ and S₂ surface states were involved in the interaction between HN₃ and the surface as suggested by the disappearance of the 0.2 and 0.8 eV peak upon dosing 2 L HN₃ on the surface at 120 K. In addition, peaks at 4.7, 6.0, 9.8 and 13.5 eV were noted, these peaks are

attributable to the 2a'', 9a', the convolution of 8a', 7a' and 1a'', and the 6a' molecular orbitals, respectively.

HN₃(DN₃) on Si(100)-2x1¹⁰

Similar experiments were carried out for HN₃(DN₃) on Si(100)-2x1. As HN₃ was dosed on the surface at 120 K, peaks at 60, 153, 163, 267 and 415 meV appeared in the HREEL spectrum. These peaks could be assigned to the HN₃ molecular vibrations. When the surface was annealed at higher temperatures, HN₃ started to desorb and to decompose. At 610 K, the HN₃ molecular characteristic peaks vanished and the spectrum was dominated by the peaks at around 110, 260 and 430 meV due to the H and NH_x (x=0,1) adspecies. Annealing the sample at T_s ~800 K caused the complete dissociation of the NH bond and the desorption of the H species as indicated by the disappearance of the Si-H and NH stretching modes at 260 and 430 meV, respectively. The decomposition process of HN₃(DN₃) on Si(100) is essentially the same as those on Si(111) and Si(100). However, a peak at ~190 meV was evident in the HREELS for HN₃ on Si(100) at 270 K, but not on Si(111). This peak could be attributed to either the NN stretching mode for the adsorbed N₂ species or the NH₂ deformation vibration. The latter species was found to be more stable on Si(100) than on Si(111). At ~1200 K, atomic N appeared to penetrate deeper into Si(100) than Si(111).

E. The 308-nm laser photodissociation of HN₃ adsorbed on Si(111)-7x7¹⁴

The 308-nm laser photodissociation of HN₃ adsorbed on Si(111)-7x7 at 100 K was investigated with HREELS and XPS. Species such as NH_x, N₂ and N₃ were identified on the surface with comparable concentrations after the irradiation with 1x10²⁰ photons of a 10 L HN₃ dosed Si(111) surface. The N₃ species showed two stretching modes at 178 and 255 meV, while that of the N₂ appeared at 208 meV in HREELS. The formation of these products was also corroborated by the corresponding XPS results. The N_{1s} XPS shifted from 399.8, 400.8 and 404.1 eV for N^I, N^{II} and N^{III} atoms in HN^IN^{II}N^{III} to 399.0, 399.0 and 403.4 eV in N^IN^{II}N^{III}, respectively. Another peak at 401.5 eV was assigned to the N₂ species on the surface. Comparing our HREELS and XPS results for N₂ on Si(111) with those for N₂ on Fe(111) and other metal surfaces allows us to conclude that the photodissociation product N₂ adsorbs on Si(111) in a side-on rather than an end-on geometry.

Further laser irradiation caused the dissociation and partial desorption of the adsorbates with NH_x species remained on the surface. The presence of the NH₂ adspecies, e.g., the 187 meV peak due to the NH₂ deformation vibration in HREELS,

suggests that the secondary reactions occurred on the surface. This was verified by the experiments carried out under the submonolayer dosage condition for the laser effect on HREELS of 0.3 L HN_3 dosed $\text{Si}(111)-7\times 7$. In this case, no obvious NH_2 and N_3 features were observed in the HREEL spectra; this suggests that the secondary reactions occurred to a far lesser extent. Annealing the post-irradiated sample to 500 and 800 K resulted in the breaking of the NH bonds and the desorption of H species, while the atomic N remained on the surface forming Si nitride. The possibility of using HN_3 for laser-induced chemical vapor deposition of Si_3N_4 and group-III nitride at low temperatures is suggested.

F. Laser-assisted chemical vapor deposition of InN on Si(100)¹²

Laser-assisted chemical vapor deposition of InN on Si(100) using HN_3 and TMIn with and without 308-nm photon excitation has been studied with XPS, UPS and SEM. No InN film could be built on the surface without 308-nm excimer laser irradiation under the present low-pressure conditions. When the photon beam was introduced, InN films with an In:N atomic ratio of 1.0 ± 0.1 and a thickness of more than 20 Å (the limit of the electron escaping depth for the In_{3d} X-ray photoelectrons) was formed at 300 and 700 K. The HeII UPS taken from the InN films agree well with the result of a pseudo-potential calculation for the InN valence band.

Our XPS measurements indicate a 3-D island growth of InN on Si(100) at 700 K, which is confirmed by the corresponding SEM images. Although the SEM taken from the same samples with 2,000 X magnification showed smooth InN films, InN islands of about 100 nm in diameter could be clearly observed with a magnification of $\geq 20,000$ X. The number of InN islands increased with prolonged film deposition time. Interestingly, the near-absence of C_{1s} signals in XP spectra suggests that the carbon contamination in the InN film is not as serious as that implied by the TMIn thermal decomposition results.

G. LPCVD of InN on GaAs²²

Recently, we have succeeded in depositing very high quality InN films on GaAs (110) substrates by low-pressure CVD using HN_3 and TMIn without laser assistance. In fact, unlike for the deposition of InN on Si described in the preceding section, laser irradiation did not promote the rate of film growth for HN_3 and TMIn. Our SEM results indicate that the films deposited on GaAs are very smooth and do not exhibit island structures when observed under 100,000 X magnification. The HeII and UPS taken from the InN film revealed distinct valence bands which agree closely with that

predicted by a pseudo-potential quantum calculation. This significant result suggests that the growth of GaN and AlN on GaAs should be quite easy if one uses HN_3 as the N-precursor.

III. PUBLICATIONS (Dec. 88-Sept. 93)

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14. Y. Bu, and M.C. Lin, "The 308-nm laser photodissociation of HN_3 adsorbed on Si(111)-7x7," Surf. Sci., in press.
15. Y. Bu, and M.C. Lin, "Surface Chemistry of N_2H_4 on Si(100)-2x1," Surf. Sci., in press.
16. Y. Bu, and M.C. Lin, "Interaction of CO with Si single crystal surfaces studied by UPS and HREELS," Surf. Sci., in press.
17. J.C.S. Chu, R. Soller, M.C. Lin and C.F. Melius, "A kinetic and mechanistic study of tetra-methyl orthosilicate decomposition reaction in the gas phase," J.A.C.S., submitted.
18. S.P. Lee and M.C. Lin, "UV photochemistry of dimethyl cadmium on a quartz substrate," Appl. Phys., submitted.
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22. Y. Bu and M.C. Lin, "LPCVD of InN on $\text{GaAs}(110)$ using HN_3 and TMIIn : Comparison with $\text{Si}(100)$ Result." *Mat. Res. Soc.*, [Proc.], submitted.

IV. PRESENTATIONS

1. "Thermal Decomposition of Tetramethyl Ortho-silicate", J. C. S. Chu, N. S. Wang and M. C. Lin, 42nd Southeast/46th Southwest Combined Regional Meeting, *Am. Chem. Soc.*, paper No. 465, Dec. 5-7, 1990, New Orleans, LA.
2. "Photodesorption and Photodissociation of Adsorbed Dimethyl Cadmium on Cold Substrates", S. -P. Lee, Y. He and M. C. Lin, 42nd Southeast/46th Southwest Combined Regional Meeting, *Am. Chem. Soc.*, paper No. 487, Dec. 5-7, 1990, New Orleans, LA.
3. "Surface Photochemistry of Tetramethyl Ortho-Silicate on Quartz and Silicon (111) Substrates", Y. He, N. S. Wang, S. -P. Lee and M. C. Lin, 42nd Southeast/46th Southwest Combined Regional Meeting, *Am. Chem. Soc.*, paper No. 488, Dec. 5-7, 1990, New Orleans, LA.
4. "Photodesorption and Photodissociation of Adsorbed Benzene by Selective Excitation at T_1 , S_1 and S_2 states", Y. Bu, S.-P. Lee and M. C. Lin, 201st ACS National Meeting, paper No. 137, Atlanta, GA., April 14-19, 1991.
5. "Thermal Decomposition of Tetraethylorthosilicate", J. S. Chu, J. Breslin and M. C. Lin, 201st ACS National Meeting, paper No. 144, Atlanta, GA., April 14-19, 1991.
6. "UV Photodesorption and Photodecomposition of Trichlorosilane Adsorbed on SiO_2 and $\text{Si}(111)$ Substrates," D. W. Shinn, S.-P. Lee and M. C. Lin, 201st ACS National Meeting, paper No. 213, Atlanta, GA., April 14-19, 1991.
7. "Laser-induced Photochemistry of Disilane on Cold Surfaces," S.-P. Lee, J. Tarr and M. C. Lin, the ILS-VII Meeting of American Physical Society, Sept. 22-26, 1991, Monterey, CA.
8. "Characterization of the Photofragmentation of Dimethyl Cadmium Adsorbed on $\text{Si}(111)$ by $\text{EI}/\text{REMPI-TOF}/\text{MS}$," S.-P. Lee and M. C. Lin, the ILS-VII Meeting of American Physical Society, Sept. 22-26, 1991, Monterey, CA.

9. "Temperature Dependence of the UPS and HREELS of HN_3 and DN_3 on Si(110)," Y. Bu, J.C.S. Chu and M.C. Lin, 21st Annual Symposium on Appl. Vac. Science and Technol., Clearwater Beach, FL, Feb. 3-5, 1992.
10. "XPS, UPS and HREELS studies of Hydrazine and Methylhydrazine on Si(111)," Y. Bu, D. Shinn and M.C. Lin, 21st Annual Symposium on Appl. Vac. Science and Technol., Clearwater Beach, FL, Feb. 3-5, 1992.
11. "Thermal Nitridation of Si(111) using Hydrazine and Hydrazoic Acid," D.W. Shinn, Y. Bu and M.C. Lin, 21st Annual Symposium on Appl. Vac. Science and Technol., Clearwater Beach, FL, Feb. 3-5, 1992.
12. "Photochemistry of Organometallics on Insulators," S.-P. Lee, J.A. Tarr and M.C. Lin, 20th Informal Conference on Photochemistry, Atlanta, GA, Apr. 26-May 1, 1992.
13. "Spectroscopy and Reactions of Hydrazoic Acid on Silicon Single Crystal Surfaces. (II). HN_3 and DN_3 on Si(100)," J.C.S. Chu, Y. Bu and M.C. Lin, 6th Int. Electronic Mat. and Proc. Conference, June 23-25, 1992, Baltimore, MD.
14. "Thermal Stability of Trimethyl Indium on Single Crystal Surfaces between 120 and 1000 K Studied by UPS, XPS and HREELS," Y. Bu and M.C. Lin, Gordon Research Conferences, High Temperature Chemistry, July 20-24, 1992, Kimball Union Academy, Meriden, NH.
15. "Thermal Stability of HN_3/DN_3 on Single Crystal Surfaces between 120 and 1350 K Studied by XPS, UPS and HREELS," Y. Bu and M.C. Lin, Gordon Research Conferences, High Temperature Chemistry, July 20-24, 1992, Kimball Union Academy, Meriden, N.H.
16. "Surface Photochemistry of Molecules Relevant to II/VI and III/V Semiconductor LCVD Processes," M.C. Lin, Workshop on Aspects of Surface Physics and Photochemistry, Hsinchu, Taiwan, June 29, 1992.
17. "Spectroscopy and Decomposition of HN_3 and N_2H_4 on Silicon Single Crystal Surfaces," M.C. Lin, Workshop on Aspects of Surface Physics and Photochemistry, Hsinchu, Taiwan, June 29, 1992.
18. "Laser-Induced Desorption of Adsorbed Molecules on Single Crystal Surfaces: From Atoms to Complex Molecules," M.C. Lin, Institute of Atomic and Molecular Sciences, Taipei, Taiwan, July 29, 1992.
19. "Spectroscopy and Reactions of HN_3 on Low-Index Silicon Surfaces," M.C. Lin, Invited lecture, International Symposium on Surface and Thin Film Science, Mar. 29-Apr. 2, 1993, Taipei, Taiwan.

20. "OMCVD of III/V Semiconductors Studied by Multiple Surface Diagnostics," M.C. Lin, Invited lecture, 1993 Annual Congress of the Royal Society of Chemistry, Apr. 5-8, 1993, Southampton, UK.
21. "Kinetics and Mechanism for the Thermal Decomposition of Tetraethyl Orthosilicate," M.C. Lin, Invited seminar, Sandia National Laboratories, Albuquerque, NM, May 13 1993.
22. "The 308-nm Laser Photodissociation of HN_3 adsorbed on $\text{Si}(111)-7\times 7$ " Y. Bu and M.C. Lin, American Vacuum Society 40th National Symposium, Nov. 15-19, 1993, Orlando, Florida.
23. "LPCVD of InN on $\text{GaAs}(110)$ Using HN_3 and TMIIn : Comparison with $\text{Si}(100)$ Results," Y. Bu and M.C. Lin, Materials Research Society Fall Meeting 1993, Nov. 29-Dec. 3, 1993, Boston, MA.

V. TECHNICAL REPORTS

1. "UV Desorption and Photochemistry of $(\text{CH}_3)_2\text{Au}(\text{hfacac})$ Adsorbed on a Quartz Substrate," A. Dagata, E. Villa and M. C. Lin, 1990.
2. "UV Photochemistry of Dimethyl Cadmium on a Quartz Substrate," S.-P. Lee and M. C. Lin, 1991.
3. "Relative Stabilities of Tetramethyl and Tetraethyl Orthosilicates in the Gas Phase," J. C. S. Chu, James Breslin, N. S. Wang and M. C. Lin, 1991.
4. Adsorption and Decomposition of Trimethyl Indium on $\text{Si}(110)$," Y. Bu, Jason C.S. Chu, D.W. Shinn and M.C. Lin, 1992.
5. "Temperature Dependence of the UPS and HREELS of HN_3 and DN_3 on $\text{Si}(110)$," Y. Bu, J. C. S. Chu and M. C. Lin, 1992.
6. Adsorption and Spectroscopy of OH and PD on $\text{Si}(110)$," Y. Bu, J.C.S. Chu and M.C. Lin, 1992.
7. "Ti - Adsorption and Thermal Decomposition of N_2H_4 and $\text{CH}_3\text{N}_2\text{H}_3$ on $\text{Si}(111)-7\times 7$," Y. Bu, D. W. Shinn and M. C. Lin, 1992.
8. "Spectroscopy and Reactions of Hydrazoic Acid on Silicon Single Crystal Surfaces (II). HN_3 and DN_3 on $\text{Si}(100)$," Jason C. S. Chu, Y. Bu and M. C. Lin, 1992.
9. "Decomposition of TMIIn on $\text{Si}(111)-7\times 7$ Studied with XPS, UPS and HREEL," Y. Bu, Jason C. S. Chu and M. C. Lin 1992.
10. "UV Photochemistry of Trivinylantimony Adsorbed on Quartz," J. A. Tarr, S.-P. Lee and M. C. Lin, 1992.

11. "Spectroscopy and Reactions of Hydrazoic Acid on Silicon Single Crystal Surfaces. (III). HN_3 and DN_3 on $\text{Si}(111)\text{-}7\times 7$," J.C.S. Chu, Y. Bu and M. C. Lin, 1993.
12. "Thermal Stability of Trimethyl Indium on $\text{Si}(100)\text{-}2\times 1$ as Studied by HREELS, UPS and XPS: A Comparison with the Results from $\text{Si}(111)\text{-}7\times 7$ and $\text{Si}(100)$ Surfaces," Y. Bu, J. C. S. Chu and M. C. Lin, 1993.
13. "UV Photochemistry of HN_3 on $\text{GaAs}(100)$," Y. Bu and M.C. Lin, 1993.
14. The Interaction of HCN/DCN with $\text{Si}(100)\text{-}2\times 1$," Y. Bu, L. Ma and M.C. Lin, 1993.
15. "The 308-nm Laser Photodissociation of HN_3 Adsorbed on $\text{Si}(111)\text{-}7\times 7$," Y. Bu and M.C. Lin, 1993.
16. "A Kinetic and Mechanistic Study of the Tetramethyl Orthosilicate Decomposition Reaction in the Gas Phase," J.C.S. Chu, R. Soller, M.C. Lin and C.F. Melius, 1993.
17. "Laser-Assisted Chemical Vapor Deposition of InN on $\text{Si}(100)$," Y. Bu, L. Ma and M.C. Lin, 1993.
18. "The 308-nm Laser Photodissociation of HN_3 Adsorbed on $\text{Si}(111)\text{-}7\times 7$," Y. Bu and M.C. Lin, 1993.
19. "The Interaction of HCN(DCN) with $\text{Si}(111)\text{-}7\times 7$ Studied with HREELS, UPS and XPS," Y. Bu, L. Ma and M.C. Lin, 1993.
20. "Thermal Dissociation of NH_2CHO (ND_2CDO) on $\text{Si}(100)\text{-}2\times 1$," Y. Bu and M.C. Lin, 1993.
21. "Nitridation of $\text{GaAs}(100)$ by Laser-Induced Decomposition of HN_3 ," Y. Bu and M.C. Lin, 1993.
22. "LPCVD of InN on $\text{Ga}(110)$ Using HN_3 and TMIIn : Comparison with $\text{Si}(100)$ Results," Y. Bu and M.C. Lin, 1993.

VI. LIST OF STUDENTS AND POSTDOCTORAL RESEARCH ASSOCIATES SUPPORTED BY THE GRANT

Graduate students:

David W. Shinn (Sep. 1989-Aug. 1992), Ph.D. candidate, to be completed
 Jason C.S. Chu (Sep. 1989-Feb. 1993), completed Ph.D. May 1993)
 Jonathan A. Tarr (Sep. 1990-Sep. 1993), Ph.D. candidate
 James Breslin (Sep. 1991-Sep. 1993), Ph.D. candidate
 Li Ma (June 11992-May 1993), Ph.D. candidate

Postdoctoral Research Associates:

S. P. Lee (Jun. 1989-May 1993)

Yue Bu (Jun. 1990-Sep. 1993)

VII. TRANSITIONS

Kinetic and mechanistic data on the thermal decomposition of tetramethyl orthosilicate and tetraethyl orthosilicate have been utilized by Sandia National Laboratories (SNL) for computer simulation of SiO_2 film deposition reactions. SNL have an ongoing collaboration with SEMITEC.

Our successful use of HN_3 as a N-precursor for InN deposition has resulted in inquiries from industrial laboratories which are involved in wide bandgap semiconductor preparation.

VIII. HIGHLIGHTS OF PUBLICATIONS, PRESENTATIONS AND AWARDS

Publications: See publications No. 3, 12, and 22 in Section III.

- A. Pub. No. 3 by Bu et al. described the stability and spectroscopy of HN_3 on Si(110), the first paper which reported the chemistry of HN_3 on Si. Its facility to decompose on the surface above 200 K suggests the potential of HN_3 for the synthesis of III-V nitrides and as a surface nitridation agent.
- B. Pub. No. 12 by Bu et al. reported the first successful synthesis of InN films on Si with $\text{In:N} = 1.0 \pm 0.1$ using HN_3 and trimethyl indium, aided by photon beam excitation. UPS analysis revealed a characteristic valence band feature of the InN crystal which agreed closely with the result of a quantum calculation using the pseudopotential method.
- C. Pub. No. 22 by Bu and Lin reported the observed rapid, linear growth of InN on GaAs(110) by low-pressure CVD using HN_3 and trimethyl indium without laser excitation or buffer layer. SEM, XPS and UPS analyses indicated the morphology and composition of InN films to be exceedingly good.

Presentations:

For our successful surface science studies of HN_3 and the syntheses of InN III/V semiconductors, we were invited by the Royal Society of Chemistry, UK, to participate in an international conference held in one of the sessions at the 1993 Annual Congress of the Royal Society of Chemistry (Apr. 1993). The focus of the meeting was

on wide bandgap semiconductors, including III/V and II/VI compounds (see Section IV, presentation No. 20).

Award:

The PI was awarded the 1989 Taiwanese-American Foundation Prize for Science and Technology for his earlier work carried out at the US Naval Research Laboratory related to studies on chemical lasers and laser applications to the chemical kinetics of gas-phase and gas-solid reactions. In 1991, he was a JSPS (Japan Society for Promotion of Science) Fellow, giving a series of lectures on gas kinetics and surface science during the summer months.